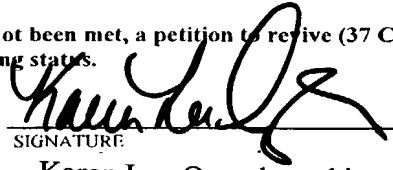


FORM PTO-1550 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 09100.025	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>10/089049</b>	
INTERNATIONAL APPLICATION NO. PCT/GB00/03775		INTERNATIONAL FILING DATE 02 October 2000		PRIORITY DATE CLAIMED 02 October 1999	
TITLE OF INVENTION MODIFIED SUPPORTED CATALYSTS FOR THE POLYMERIZATION OF OLEFINS					
APPLICANT(S) FOR DO/EO/US Eberhard ERNST et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.					
2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.					
3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.					
4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).					
5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))					
a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).					
b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.					
c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).					
6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).					
a. <input type="checkbox"/> is attached hereto.					
b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).					
7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))					
a. <input checked="" type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).					
b. <input checked="" type="checkbox"/> have been communicated by the International Bureau.					
c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.					
d. <input type="checkbox"/> have not been made and will not be made.					
8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).					
9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).					
10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).					
Items 11 to 20 below concern document(s) or information included:					
11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.					
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.					
13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.					
14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.					
15. <input type="checkbox"/> A substitute specification.					
16. <input type="checkbox"/> A change of power of attorney and/or address letter.					
17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.					
18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).					
19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).					
20. <input type="checkbox"/> Other items or information:					

U.S. APPLICATION NO. (37 CFR 1.53) <b>10/089049</b>		INTERNATIONAL APPLICATION NO <b>PCT/GB00/03775</b>		ATTORNEY'S DOCKET NUMBER <b>09100.025</b>		
21. <input type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. .... <b>\$1000.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$860.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$710.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$690.00</b> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>		
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	860.00	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$		
Total claims	- 20 =		x \$18.00	\$		
Independent claims	- 3 =		x \$80.00	\$		
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	990.00	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$		
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$		
<b>SUBTOTAL =</b>				\$	990.00	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$		
<b>TOTAL NATIONAL FEE =</b>				\$	990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$		
<b>TOTAL FEES ENCLOSED =</b>				\$	990.00	
				Amount to be refunded:	\$	
				charged:	\$	
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>990.00</u> to cover the above fees is enclosed.						
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.						
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0548. A duplicate copy of this sheet is enclosed.						
d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card          information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.						
<b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.						
SEND ALL CORRESPONDENCE TO  Karen Lee Orzechowski LINIAK, BERENATO, LONGACRE & WHITE 6550 Rock Spring Drive, Suite 240 Bethesda, MD 20817 Telephone: (301) 896-0600 Facsimile: (301) 896-0607						
				 SIGNATURE		
				Karen Lee Orzechowski NAME		
				Registration No. 31,621 REGISTRATION NUMBER		

Attorney's Docket No. 09100.025

PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re: EBERHARD ERNST  
Appl. No.: [National Stage of PCT/GB00/03775] Group Art Unit: [Not Assigned]  
Filed: March 25, 2002 Examiner: [Not Assigned]  
For: MODIFIED SUPPORTED CATALYSTS FOR THE POLYMERIZATION  
OF OLEFINS

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

Prior to calculating the filing fee for the above-identified patent application, please amend the application as follows:

In the Claims:

Please amend claims 3 and 4 to read as follows:

3. (Amended) The process as claimed in claim 1 comprising two or more metallocenes forming a multi-site catalyst.

4. (Amended) The process as claimed in claim 1 wherein the pre-polymerization olefin or olefin mixture is one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

6. (Amended) The process as claimed in claim 1 wherein the support material is silica.

8. (Amended) The process as claimed in claim 1, wherein the pre-polymerization is carried out in gas phase.

**Please add new claims 10- 21 as follows:**

11. (New) The process as claimed in claim 2 wherein the pre-polymerization olefin or olefin mixture is one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

12. (New) The process as claimed in claim 3 wherein the pre-polymerization olefin or olefin mixture is one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

13. (New) The process as claimed in claim 10 wherein the pre-polymerization olefin or olefin mixture is one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

14. (New) The process as claimed in claim 7, wherein the pre-polymerization is carried out in gas phase.

15. (New) The process as claimed in claim 7, wherein the pre-polymerization is slurry phase polymerization in an oil or grease slurry medium.

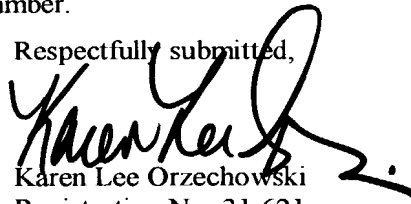
Preliminary Amendment  
 Application No. [National Stage of PCT/GB00/03775]  
 Filing Date: March 25, 2002  
 Page 3 of 3

REMARKS

These amendments are made solely for the purposes of eliminating multiple dependencies. No new matter has been added.

Should the Examiner has any questions or wishes to discuss this application, kindly telephone the undersigned at the below-listed number.

Respectfully submitted,

  
 Karen Lee Orzechowski  
 Registration No. 31,621

Date: March 25, 2002

LINIAK, BERENATO, LONGACRE & WHITE  
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CERTIFICATION OF FACSIMILE TRANSMISSION	CERTIFICATE OF MAILING
<p>I hereby certify that this paper is being facsimile transmitted to the Patent and Trademark Office at Fax No. (703) 308-2742 on March 25, 2002.</p> <p>_____                      Karen Lee Orzechowski</p>	<p>I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Assistant Commissioner For Patents, Washington, DC 20231, on March 25, 2002.</p> <p>_____                      Karen Lee Orzechowski</p>

3. (Amended) The process as claimed in claim 1 [or 2] comprising two or more metallocenes forming a multi-site catalyst.

4. (Amended) The process as claimed in claim 1 [claims 1 to 3] wherein the pre-polymerization olefin or olefin mixture is one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

6. (Amended) The process as claimed in claim 1 [claims 1 to 5] wherein the support material is silica.

8. (Amended) The process as claimed in claim 1 [to7], wherein the pre-polymerization is carried out in gas phase.

9. (Amended) The process as claimed in claim 1 [to7], wherein the pre-polymerization is slurry phase polymerization in an oil or grease slurry medium.

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Modified Supported Catalysts  
for the Polymerization of Olefins

The invention relates to modified supported catalysts for the polymerization of olefins, for example based on single-site and multi-site metallocene catalysts, supported on inorganic or organic supports, or based on the Ziegler-Natta type catalysts.

Metallocenes of the metals of e.g. transition group IV of the Periodic Table of the elements are highly active catalysts for the polymerization of olefins. The resulting polyolefins have new advantageous combinations and supplement the product range of the polyolefins prepared hitherto using known conventional Ziegler-Natta catalysts.

It is known that catalysts based on unbridged, substituted and unsubstituted biscyclopentadienyl metallocenes in combination with aluminoxanes as cocatalyst can be used for the preparation of polyethylene and ethylene-olefin copolymers (EP 0 128 046).

It is also known that stereoregular polyolefins can be prepared using bridged, chiral metallocenes. For bridging the ligand systems, use is mostly made of dimethylsilanediyl groups (EP 0 316 155), methylphenylsilanediyl groups (EP 0 320 762), ethylene groups (Brintzinger, J. Organomet. Chem. 288 (1985), 63-67) isopropylidene bridges (EP 0 459 264) and silyl-substituted diyl bridges (WO 97 02 276).

Depending on the ligand type and the substituents, isotactic, syndiotactic, hemiisotactic, stereoblock-type and atactic homopolymers and copolymers having aliphatic

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or cyclic structures can be prepared.

As ligands, preference is given to using substituted and unsubstituted cyclopentadienyl units (EP 316 155), substituted and unsubstituted indenyl units (EP 0 302 424; EP 0 485 823) and also substituted and unsubstituted cyclopentadienyl units in combination with unsubstituted fluorenyl groups (EP 0 412 416).

It is further known that bridged metallocenes having a cyclopentadienyl system and a heteroatom ligand (constrained geometry catalyst) can also be used for the polymerization of olefins (US 5 096 867).

A disadvantage of such homogeneous catalysts in the polymerization of olefins are the resulting powders, having only a low bulk density. The particle morphology of such products can in principle be somewhat improved by a specific pretreatment of the metallocene with the cocatalyst (EP 0 302 424). However, such a process has the disadvantage of, in particular, heavy deposit formation in industrial reactors (EP 0 563 917).

Although the use of methylaluminoxane, which is insoluble in aliphatic solvents, as support material gives a certain improvement in the activity and likewise leads to pulverulent products [Polymer 32(1991), 2671-2673].

Supporting the metallocene on oxidic materials such as silicon oxide or aluminium oxide with pretreatment of the starting material, which may be partially dehydrated, with the cocatalyst is a known method (WO 91 09 882) used in homopolymerization and copolymerization of ethylene. However, in this method, the particle size of the polymer particle is determined essentially by the particle size of the support material.



Further processes describe the modification of the oxidic support using methylaluminoxanes and the subsequent application of the metallocene (EP 0 206 794). However, this method restricts the ability to control the particle size by means of the properties of the support materials.

EP 0 685 494 describes a further supported catalyst which is prepared by the application of methylaluminoxane to a hydrophilic oxide, subsequent crosslinking of the methylaluminoxane using a polyfunctional organic crosslinker and subsequent application of an activated methylaluminoxane/metallocene complex. The disadvantage of this supported catalyst is that at the relatively high polymerization conversions achieved in industrial plants, the strength of the supported catalysts is not sufficient to ensure a compact, granular morphology of the polymer product.

A support material by drying hydrophilic inorganic oxides and reacting with aluminoxanes and polyfunctional crosslinkers gives, after contacting with catalysts, a supported catalyst system for a stable high bulk density in olefin polymerization even at high conversion rates (EP 0 787 746).

Methods for modifying homogeneous catalysts and supported catalyst systems by pre-polymerization are also known.

In EP 0 354 893 a homogeneous catalyst is prepared by pre-polymerizing a precipitated complex of an aluminium alkyl and a metallocene catalyst with an olefin monomer at a temperature below the polymerization temperature of the monomer, followed by polymerizing the olefin monomer under polymerization conditions. EP 0 426 638 describes the pre-polymerization of propylene in combination with



supported catalyst for liquid-phase polymerization of olefins for the production of high molecular weight polyolefins without reactor fouling, formation of polymer fines resulting from soluble catalyst components and disrupted catalyst components in the initial phase of the olefin polymerization.

It has now surprisingly been found, that these requirements are achieved by a modified supported olefin polymerization catalyst, characterised in that the catalyst is modified by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization.

The supported catalyst may be a metallocene catalyst, for example with one, two or three  $\eta^5$  ligands bonding to a transition metal or lanthanide, preferably one or two  $\eta^5$  ligands such as cyclopentadienyl, indenyl or fluorenyl. The  $\eta^5$  ligands may be linked to each other by bridging groups, for example to yield a bridged bis- $\eta^5$  ligand. Where only one  $\eta^5$  ligand is bonded to the metal, a pendant group on the ligand can also form a  $\sigma$  bond to the metal, a so-called "scorpionate" catalyst.

Ziegler-Natta catalysts are well known, and the invention may also be useful with other catalysts such as Philips ( $\text{CrO}_x$ ) catalysts.

Metallocene catalysts may be classified as single-site or multi-site. Both may be coactivated by a cocatalyst, for example methyl aluminoxane, and may be supported on an inorganic or organic carrier. Ziegler-Natta catalysts, which are well known as multi-site catalysts, are supported by their nature.

The olefin used for the polymerization, different from the olefin of the subsequent polymerization, may be one

or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 3-methyl-1-pentene, 3-methyl-1-hexene, 3,4-dimethyl-1-pentene, 3,4-dimethyl-1-hexene, 1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,5-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4,4-dimethyl-1-hexene, 6,6-dimethyl-1-heptene, vinyl cyclopropane, vinyl cyclobutane, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, vinyl cyclooctane, allyl cyclopropane, allyl cyclobutane, allyl cyclopentane, allyl cyclohexane, allyl cycloheptane or allyl cyclooctane.

Preferred are one or more of propylene, 1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane, vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane, whilst particularly preferred olefins are 3-methyl-1-butene, 4-methyl-1-pentene, vinyl cyclopentane and vinyl cyclohexane.

Typically the pre-polymerization will result in 0.001 - 5.0, e.g. 0.001 - 3.0 or 0.01 - 1.0 parts by weight relative to the catalyst and support of the polyolefin or olefin copolymer different from the polyolefin or olefin copolymer of the subsequent olefin polymerization.

The melting point or softening point of the polyolefin or olefin copolymer resulting from pre-polymerization is suitably at least 20°C, preferably 30°C higher than the melting point or softening point of the polyolefin or olefin copolymer of the subsequent olefin polymerization.

One particular supported metallocene catalyst for olefin polymerization which may be modified according to the

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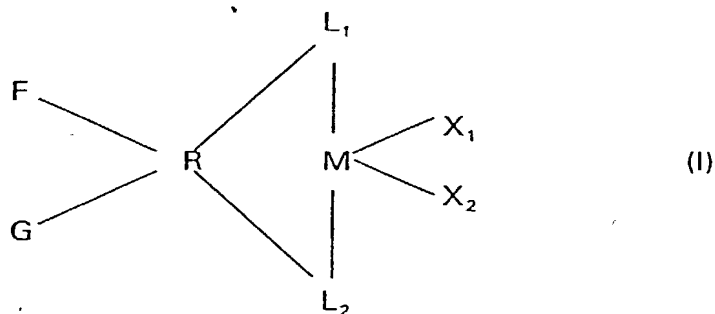
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- 7 -

invention, especially for liquid-phase polymerization of olefins, comprises

A) 90.0 - 99.9 parts by weight of a catalyst support based on a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof, which catalyst support is obtainable by simultaneous reaction with aluminoxanes and with polyfunctional organic crosslinkers,

B) 10-0.1 parts by weight of a metallocene compound of the formula I



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X<sub>1</sub> and X<sub>2</sub> are identical or different and are each a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>20</sub>-alkylaryl group, a C<sub>7</sub>-C<sub>20</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>20</sub>-arylalkenyl group, hydrogen or a halogen atom,

L<sub>1</sub> and L<sub>2</sub> are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M, R is carbon, silicon, germanium or tin, F and G are identical or different and



According to the invention, suitable polyfunctional organic crosslinkers in the catalyst support are all organic compounds having more than one functional group which can react with metal-carbon bond. Preference is given to using a bifunctional crosslinker. Such bifunctional organic compounds can be, for example, aliphatic or aromatic diols, aldehydes, dicarboxylic

acids, primary or secondary diamines, diepoxy compounds. Most preference is given to using aliphatic and aromatic diols, secondary amines or diepoxy compounds or mixtures thereof. Particular preference is given to using ethylene glycol, butanediol, bisphenol A and 1,4-butanediol diglycidyl ether. Tri- or higher functional crosslinkers which can be used are, for example, triethanolamine, glycerol, phloroglucinol or tetraethylenepentamine.

The molar ratio between the aluminium as aluminosilane and the polyfunctional organic compound in the catalyst support can vary within a wide range and is between 1 and 100, preferably between 1 and 40. Higher molar ratios of aluminium to polyfunctional organic compound are used particularly when use is made of tri- or higher-functional crosslinkers which can form a correspondingly higher number of crosslinks.

According to the invention, preferred ligands  $L_1$  and/or  $L_2$  in the metallocene compound are substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl radicals. Particular preference is given to cyclopentadienyl, tetramethylcyclopentadienyl, indenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, 2-methyl-4,5-benzindenyl and fluorenyl units and also ferrocene- and ruthenocene-substituted units as are described, for example, in EP 0 673 946.

According to the invention, the following metallocenes are particularly preferred:

bis(trimethylsilyl) silanediylbicyclopentadienyl-zirconium dichloride,  
bis(trimethylsilyl) silanediyl-diindenylzirconium dichloride,  
bis(trimethylsilyl) silanediylbis (2-methylindenyl) zirconium dichloride,



bis(trimethylsilyl) silanediylbis (2-methyl-4, 5-  
 benzoindenyl) zirconium dichloride,  
 bis(trimethylsilyl) silanediylbis (2-methyl-4-  
 phenylindenyl) zirconium dichloride,  
 bis(trimethylsilyl) silanediylbis (2-methyl-4-  
 naphthylindenyl) zirconium dichloride,  
 bis(trimethylsilyl) silanediyl difluorenylzirconium  
 dichloride,  
 bis(trimethylsilyl) silanediyl (fluorenyl)  
 (cyclopentadienyl) zirconium dichloride,  
 bis(trimethylsilyl) silanediyl (fluorenyl) (indenyl)  
 zirconium dichloride,  
 bis(trimethylsilyl) silanediyl (tetramethylcyclopenta-  
 dienyl) (indenyl) zirconium dichloride,  
 methyl (trimethylsilyl)  
 silanediyl dicyclopentadienylzirconium dichloride,  
 methyl (trimethylsilyl) silanediyl diindenylzirconium  
 dichloride,  
 methyl (trimethylsilyl) silanediylbis (2-methylindenyl)  
 zirconium dichloride,  
 methyl (trimethylsilyl) silanediylbis (2-methyl-4,5-  
 benzoindenyl) zirconium dichloride,  
 methyl (trimethylsilyl) silanediylbis (2-methyl-4-  
 phenylindenyl) zirconium dichloride,  
 methyl (trimethylsilyl) silanediylbis (2-methyl-4-  
 naphthylindenyl) zirconium dichloride,  
 methyl (trimethylsilyl) silanediyl difluorenylzirconium  
 dichloride,  
 methyl (trimethylsilyl) silanediyl (fluorenyl)  
 (cyclopentadienyl) zirconium dichloride,  
 methyl (trimethylsilyl) silanediyl (fluorenyl) (indenyl)  
 zirconium dichloride and  
 methyl (trimethylsilyl) silanediyl (tetramethylcyclo-  
 pentadienyl) (indenyl) zirconium dichloride.

According to the invention, in the metallocene compound  
 in addition also amido, phosphido and arsenido radicals

can be used as ligands  $L_2$ , where the substituents of these ligands are as defined for  $X_1$  and  $X_2$ , or substituted or fused ferrocenyl- or ruthenocenyl-radicals.

The invention further provides a process for preparing the modified supported catalyst as hereinbefore described, comprising the step of modifying a supported olefin polymerization catalyst by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization, whereby the melting point or softening point of the polyolefin or olefin copolymer resulting from pre-polymerization is at least 20°C, preferably 30°C higher than the melting point or softening point of the polyolefin or olefin copolymer, of the subsequent olefin polymerization.

The modified catalyst may be isolated from the modification medium prior to use in the subsequent polymerization reaction.

In particular, a process for preparing a modified supported metallocene catalyst for polymerization of olefins, especially in liquid phase, comprises the steps:

α) preparing a catalyst support A) by

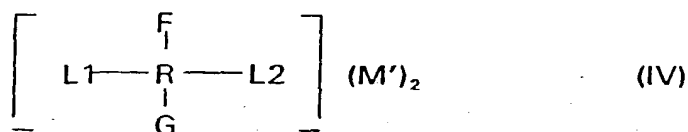
α1) drying a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof at from 110 to 900°C, e.g. 110 to 800°C, subsequently

α2) if desired, reacting the free hydroxyl groups of the oxide completely or partially with aluminoxanes or aluminium alkyls and subsequently

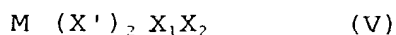
F and G are identical or different and are each a trimethylsilyl radical of the formula  $-\text{Si}(\text{CH}_3)_3$ , where G may also be a  $\text{C}_1$ - $\text{C}_{10}$ -alkyl radical, preferably a alkyl



According to the invention, in stage  $\alpha 3$ ) for preparing the catalyst support, the metering in of the solutions is carried out simultaneously and continuously and the crosslinker solution may be heated or cooled if desired. The temperature to which the solution is heated or



where  $L_1$ ,  $L_2$ , F, G and R are as defined for the formula I and M' is an alkali metal, preferably lithium, with a compound of the formula V



Where M,  $X_1$  and  $X_2$  are as defined for the formula I and  $X'$  is a halogen atom, preferably chlorine.

Preparing the metallocene compounds B), the reaction of the dimetallated compound of the formula IV with the metal halide of the formula V can be carried out, for example, as described in EP 0 659 756. However, the reaction of the dimetallated compound of the formula IV with the metal halide of the formula V is advantageously carried out in solvent mixtures of aromatic and/or aliphatic hydrocarbons, which may also be halogenated, with dialkyl ethers, preferably alkane/ether mixtures such as, for example, hexane/ether mixtures. Aliphatic hydrocarbons can be, for example, all  $C_5$ - $C_{12}$ -alkanes. Preference is given to n-pentane, n-hexane, n-heptane or cyclohexane. Among the dialkylethers, preference is given to all di- $C_2$ - $C_4$ -alkyl ethers, for example diethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether or tert-butyl-methyl ether. Examples of suitable halogenated hydrocarbons are all  $C_1$ - $C_4$ -chloroalkanes. Particular preference is given to dichloromethane.

The preparation of the supported metallocene catalyst according to  $\beta$  is carried out by suspending the catalyst support A) in an inert hydrocarbon, preferably toluene, and bringing it into contact with the metallocene compound B). In this procedure, the metallocene compound is dissolved, for example, in an inert hydrocarbon. Inert solvents which can be used are, for example, aliphatic or aromatic hydrocarbons, preferably toluene. The metallocene compounds B) are preferably

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used in an amount of from 0.3 wt % to 5 wt % based on the total mass of the supported catalyst. The mixing time is from 5 minutes to 24 hours, preferably from 1 to 12 hours. The mixing is carried out at a temperature of from -10 to +80°C, in particular from 20 to 70°C. The application of the metallocene compound B) is preferably carried out subsequent to the synthesis of the support A) in order to save a drying step. After the reaction is complete, the solvent is decanted and taken off under reduced pressure until a free-flowing solid remains.

According to the invention the pre-polymerization of the supported catalyst is carried out in absence of a solvent or in an inert hydrocarbon solvent. The pre-polymerization temperature is from particularly -20 to 95°C, preferably from 0 to 60°C. The treatment of the supported catalyst may be carried out under reduced, atmospheric or elevated pressure batchwise or continuously.

In a preferred embodiment the monomer feed during pre-polymerization reaction is at a rate from 0.05 to 20 g monomer/g supported catalyst/h, more preferably from 0.5 to 2 g monomer/g supported catalyst/h.

According to the invention, the pre-polymerization of these monomers in presence of the supported catalyst is carried out preferably in gas phase, although pre-polymerization by pore filling of a dry porous catalyst with liquid monomer, by slurry phase polymerization using oil or grease as a slurry medium or by slurry phase polymerization using an evaporatable hydrocarbon as slurry medium are also possible.

In a preferred embodiment especially for liquid-phase polymerization of propylene, the modification of the



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supported metallocene catalyst is carried out by pre-polymerization of 4-methyl-1-pentene.

The modified supported catalyst of the invention is polymerization-active without further activating additives. However, it has been found to be particularly advantageous to use aluminium alkyls, preferably trimethylaluminium, triethylaluminium or triisobutylaluminium, as scavenger and as additional activator. The amount is, based on the aluminium, 50 - 5000 mol, preferably 100 - 500 mol, per mol transition metal of the metallocene compound in the modified supported catalyst.

According to the invention the modified supported catalysts may be used for the polymerization of olefins or olefin mixtures, in particular  $C_2$ - $C_{16}$ - $\alpha$ -olefins, preferably ethylene, propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, cyclopentene, norbornene and/or norbornadiene. The modified supported catalysts make possible the preparation of homopolymers, copolymers and heterophasic copolymers. Most preferred is the use of the modified supported catalysts for the polymerization of propylene.

The invention further provides a process for preparing polyolefins by polymerization or copolymerization of olefins, wherein the polymerization catalyst used is a modified supported catalyst according to the invention.

In liquid phase polymerization, it is possible to use inert solvents, for example, aliphatic or cycloaliphatic hydrocarbons such as pentane, hexane or cyclohexane; toluene can also be used. Preference is given to carrying out the polymerization in the liquid monomer.

If required, hydrogen is added as molecular weight

regulator. The total pressure in the polymerization is usually 0.5 - 150 bar. Polymerization is preferably carried out in the pressure range of 1 - 40 bar.

In the copolymerization of ethylene with propylene, the polymerization is preferably carried out in liquid propylene or in hexane as suspension medium. In the polymerization in liquid propylene, the ethylene is preferably fed in an amount such that a partial pressure ratio  $P_{\text{propylene}}/P_{\text{ethylene}} > 0.5$ , in particular  $> 1.0$ , is established over the liquid phase ( $P_{\text{ethylene}}$  = partial pressure of the ethylene in the gas phase over the suspension;  $P_{\text{propylene}}$  partial pressure of the propylene in the gas phase over the suspension). In the copolymerization in hexane as suspension medium, an ethylene/propylene gas mixture having a propylene content of from 1 to 50 mol%, preferably from 5 to 30 mol%, is fed in. The total pressure is kept constant during the polymerization by metering in a further amount. The total pressure is from 0.5 to 40 bar, preferably from 1 to 20 bar. The polymerization time is from 10 minutes to 6 hours, preferably from 30 minutes to 2 hours.

The modified supported catalysts make possible the preparation of high molecular weight polyolefins and olefin copolymers without reactor fouling, without formation of polymer fines resulting from soluble catalyst components and disrupted catalyst components in the initial phase of the olefin polymerization, especially under technical liquid polymerization conditions. Particle size and particle size distribution may be controlled in all stages of polymerization process. The polyolefins and olefin copolymers are obtained in granular form even at high polymerization conversions, they have a high bulk density and a low fines content.

The following examples illustrate the invention.

Abbreviations used are:

$^{13}\text{C-NMR}$	$^{13}\text{C}$ nuclear magnetic resonance spectroscopy
$d_{50}$	Mean particle diameter determined by sieve analysis
$^1\text{H-NMR}$	$^1\text{H}$ nuclear magnetic resonance spectroscopy
$M_w$	Weight average molar mass in g/mol determined by GPC
$M_n$	Number average molar mass in g/mol determined by GPC
$M_w/M_n$	Polydispersity
MAO	Methylaluminoxane
MC	Metallocene compound MS mass spectrometry
$T_m$	Melting point determined by DSC
$\text{cat}_{\text{pure}}$	supported catalyst without pre-polymer
$\text{cat}_{\text{pre-pol}}$	p re-polymerized catalyst
$m_{\text{cat}}$	weight of the supported catalyst
$m_{\text{pre-pol}}$	weight of the pre-polymer
TEAL	triethyl aluminium
MFR	melt flow rate of PP in g/10 min measured at 230°C using a weight of 2.16 kg
$\text{MFR}_2$	melt flow rate of PE in g/10 min measured at 190°C using a weight of 2.16 kg
$\text{MFR}_{21}$	melt flow rate of PE in g/10 min measured at 190°C using a weight of 21.6 kg
XS	amount of polymer still soluble in xylene at 25 C after precipitation from high temperature solution

## Example 1

## Preparation of the catalyst support

The silica (pore volume 1.58 cm<sup>3</sup>/g; surface area 300 m<sup>2</sup>/g) was dried at 200°C using the procedure described in EP 787 746 Example 1. The OH content was 2.05 mmol/g SiO<sub>2</sub>.

109.1 g of the dried oxide were suspended in 1.41 of dry toluene in a three-neck flask equipped with a stirrer and two dropping funnels. In the first dropping funnel, 252 g (1298.3 mmol of Al) of a 30% strength solution of methylaluminoxane (MAO) in toluene were mixed with 740 ml of toluene and the second dropping funnel was charged with a solution of 12.25 g bisphenol A (53.72 mmol) in 613 ml oxygen-free toluene.

After 127.5 ml of the MAO solution had been initially introduced into the suspension at 55°C within 15 minutes under moderate stirring, the two solutions were simultaneously added dropwise within approximately 40 minutes. The stirrer speed during this procedure was 200 rpm. The rate of dropwise addition was low and was selected such that both solutions were consumed at a suitable decrease in volume. The suspension was subsequently stirred for further three hours at 55°C and was then allowed to stand. A fine white solid settled out. After pressurizing with 0.3 bar nitrogen, the cold suspension was stored for at least three weeks.

Subsequently the supernatant toluene was removed, the residue was again taken up two times with 800 ml toluene and washed for 15 minutes at 70°C. After separation of the white solid the supernatant washing solutions were removed. The resulting catalyst support suspension was directly used for the catalyst preparation.

A suspension of 21.0 g of zirconium tetrachloride in 300 ml of absolute n-hexane is added at  $-80^{\circ}\text{C}$  to a solution of 46.6 g of the dilithium salt in 300 ml of absolute diethyl ether. After warming to room temperature over a period of two hours, the mixture is stirred for 20 hours at room temperature. After taking off the solvent in a high vacuum, the solid residue is washed twice with 100 ml absolute diethyl ether. The ether fractions are collected, the solvent is evaporated to a residual volume of 100 ml and the solution is cooled to  $-30^{\circ}\text{C}$  for a few days, yielding an amorphous product which is isolated by filtration. After 3 hours drying in vacuum, a 10.0 g amount of pseudoracemethyl(trimethylsilyl)-silanediyl(2-methyl-4-phenylindenyl) zirconium dichloride (16.0 % yield) is obtained. After further recrystallization from diethylether at  $30^{\circ}\text{C}$  a purity of

438 mg of the supported metallocene catalyst prepared in Example 3 were placed in the catalyst feeder.

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Subsequently the powder was rinsed into the reactor using a further 500 g of propylene, the stirrer speed was increased to 400 rpm, the mixture was heated over a period of 12 minutes to the polymerization temperature of 70°C and the temperature was kept constant. The reaction was stopped after two hours by flashing off the propylene. This gave 109.5 g of polypropylene with a fines content (<100  $\mu\text{m}$ ) determined by sieve analysis of 3.8 % by weight. The activity was 0.25 kg/g cat<sub>pure</sub> x 2 h. The polymer particles were granular ( $M_w$  = 604 kg/mol; polydispersity 2.9;  $T_m$  = 153°C) and the reactor showed deposits on the stirrer, the thermocouple and the wall above the liquid phase.

#### Example 5

##### Modification of the supported metallocene catalyst by pre-polymerization

A modified thin-film evaporator was used for the pre-polymerisation. The evaporator was placed in a glove box and equipped with a powder flask that contained the catalyst powder. The system was connected with a second flask filled with oxygen and moisture free 4-methyl-1-pentene. 10 g of the catalyst prepared in example 3 were placed in the powder flask. The pressure was reduced to the vapour pressure of the monomer. 0.1 bar hydrogen was added. The polymerization conversion was followed by weighing the flask. After a polymerization time of one hour the weight ratio pre-polymer to catalyst ( $m_{\text{pre-pol}}/m_{\text{cat}}$ ) was 0.4. Softening of the pre-polymer began at a temperature of 234°C.

#### Example 6

##### Propylene polymerization using the supported metallocene catalyst

A 20 l stirred reactor was, after being made inert with

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nitrogen, charged at room temperature with 6.5 kg of liquid propylene, 2 l hydrogen and with a 1 molar triethylaluminum/hexane solution and the mixture was stirred for 15 minutes at 200 rpm. The triethylaluminum/hexane solution was fed in such an amount that a TEAL/Zr molar ratio of 600 was adjusted.

260 mg of the unmodified supported metallocene catalyst prepared according to Example 3 were mixed with the co-catalyst for 15 minutes. Subsequently the mixture was rinsed into the reactor using a further 500 g of propylene, the stirrer speed was increased to 400 rpm, the mixture was heated over a period of 12 minutes to the polymerization temperature of 70°C and the temperature was kept constant. The reaction was stopped after two hours by flashing off the propylene. This gave 1536 g of polypropylene with a fines content (<100 µm) determined by sieve analysis, of 5 % by weight. The activity was 5.9 kg / g cat<sub>pure</sub> x 2h. The polymer particles were granular (M<sub>w</sub> = 345 kg/mol; polydispersity 2.9; T<sub>m</sub> = 153°C) and the reactor showed deposits on stirrer, thermocouple and the wall above the liquid phase.

#### Example 7

Propylene polymerization using a 4-methyl-1-pentene pre-polymerized catalyst

The polymerisation was carried out by the method described in Example 6, but using 445 mg of the pre-polymerized catalyst of Example 5.

This gave 1938 g of polypropylene with a fines content (<100 µm) determined by sieve analysis of 1.2 % by weight. The activity was 4.4 kg/g cat<sub>pre-pol</sub> x 2h (6.1 kg/g cat<sub>pure</sub> x 2h). The polymer particles were granular (M<sub>w</sub> = 324 kg/mol; polydispersity 2.8; T<sub>m</sub> = 153°C) and the





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This gave 1184 g of polypropylene with a fines content ( $<100\ \mu\text{m}$ ) determined by sieve analysis of 0.9 % by weight. The activity was  $2.2\ \text{kg/g cat}_{\text{pre-pol}} \times 2\text{h}$  ( $2.6\ \text{kg/g cat}_{\text{pure}} \times 2\text{h}$ ). The polymer particles were granular ( $M_w = 336\ \text{kg/mol}$ ; polydispersity 2.8;  $T_m = 153^\circ\text{C}$ ) and the reactor showed no deposits on the internal fittings or the wall.

#### Example 10

Propylene copolymerization using a 4-methyl-1-pentene pre-polymerized catalyst

The pre-polymerization was carried out by the method described in Example 5. The weight ratio pre-polymer to catalyst ( $m_{\text{pre-pol}}/m_{\text{cat}}$ ) was 0.8. Softening of the pre-polymer began at a temperature of  $232^\circ\text{C}$ .

The 20 l stirred polymerization reactor was, after being made inert, charged at room temperature with 6.5 kg of liquid propylene, 85 g ethylene, 2 l hydrogen and with a 1 molar triethylaluminum/hexane solution and the mixture was stirred 15 minutes at 200 rpm. The triethylaluminum/hexane solution was fed in such an amount that a TEAL/Zr mole ratio of 600 was adjusted.

The polymerization reactor was charged with 295 mg of the pre-polymerized catalyst.

The reaction was terminated after 30 minutes to limit the extent of conversion. The polymerization run gave 607 g of polypropylene copolymer with a fines content ( $<100\ \mu\text{m}$ ) determined by sieve analysis of 1.6 % by weight. The activity was  $5.8\ \text{kg/g cat}_{\text{pre-pol}} \times 2\text{h}$  ( $10.4\ \text{kg/g cat}_{\text{pure}} \times 2\text{h}$ ). The polymer particles were granular ( $M_w = 280\ \text{kg/mol}$ ; polydispersity 2.8;  $T_m = 142^\circ\text{C}$ ) and the reactor showed no deposits on the internal fittings or the wall.

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## Example 11

Mono-site catalyst based on  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-2-Ind})_2\text{ZrCl}_2$  and MAO

96 g  $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-2-Ind})_2\text{ZrCl}_2$  (as can be obtained from Boulder Scientific Company) and 8.6 kg toluene solution of 30 wt% MAO (as can be obtained from Albermarle) were mixed until solution and activation of the metallocene complex, and added slowly to 7 kg of silica, grade Sylopol 2104 (obtained from Grace), calcined at 800°C. The amount of liquid was less than the silica pore volume, hence the silica powder remained free floating and stirrable. The formed mono-site catalyst was dried under nitrogen to a toluene residual amount of 0.45 wt%, having bulk density of 330 kg/m<sup>3</sup>.

## Example 12

Prepolymerization using propylene

333 g of supported catalyst, Example 11, was placed in an inerted glass vessel, volume 3000 mL, equipped with a Teflon bladed stirrer. The vessel was connected to a steel cylinder containing a preweighed amount of liquid propylene. The catalyst vessel nitrogen atmosphere was replaced by gaseous propylene, and pressure from the propylene cylinder adjusted to 0.6 bar. The pressure was increased up to 1.5 bar during 3 hours 15 min at ambient temperature, until the propylene cylinder was emptied. Weight of resulting prepolymerised catalyst was 424 g. The procedure was repeated for another two batches of catalyst, giving overall 1274 g prepolymerised catalyst from 963 g of pure catalyst.

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## Example 13

## Prepolymerisation using 4-Me-1-pentene

332 g of supported catalyst, Example 11, was placed in an inerted glass vessel, volume 3000 mL, equipped with a Teflon bladed stirrer. The vessel was connected to another glass bottle containing 4-Me-1-pentene. The catalyst vessel was evacuated twice, each time refilled with gaseous 4-Me-1-pentene boiling off from the bottle, to substitute the nitrogen atmosphere. The 4-Me-1-pentene pressure in the catalyst vessel was then kept at 0.5 to 0.7 bar at ambient temperature for 4 hours, resulting in 449 g of prepolymerised catalyst. The procedure was repeated for another two batches of catalyst, giving overall 1330 g prepolymerised catalyst from 972 g of pure catalyst.

## Example 14

## Polymerisation of non batch prepolymerised catalyst in Example 11

The catalyst prepared in Example 11 was dispersed to a 153 g/l oil/grease mixture (80+20 vol% of "Parafinium Liquidum 68" from Technol and "Vaselinfett Album" from Technol). The catalyst mud was then fed to a continuous process of two reactors in series: bulk propylene prepolymerisation (9 min residence time at 20°C) and loop bulk propylene polymerisation (1.9 h residence time at 70°C), 585 ppm of hydrogen and 0.1 g/kgpropylene of triethyl aluminum were present.

The catalyst productivity became 6.2 kg/gCat, or 3.2 kg/gCat\*h. Process operability was bad. Inspection of the polymerisation reactor inner surface after 38 hours of operation showed sheeting and plugging from this catalyst. The powder samples, taken out of the lots and from the reactor, contained flat irregular shaped

The catalyst productivity became  $4.8 \text{ kg/gCat}_{\text{pure}}$ , or  $3.5 \text{ kg/gCat}_{\text{pure}} \cdot \text{h}$ . Process operability was bad, although less severe than in Example 14. Inspection of the polymerisation reactor inner surface after 46 hours of operation showed plugging from this catalyst, but no sheeting and only few fine particle residues. The powder samples, taken out of the lots and from the reactor, contained flat irregular shaped agglomerates with a diameter up to 1.5 cm. They appeared as sintered particles containing also fines. After reaching the target loop density these agglomerates caused loop reactor discharge problems.

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Transparency and partly fused surface of particles were also observed. Product polymer analyses showed MFR = 38, XS = 1.6 wt%. Polymer powder bulk density was 0.434 g/ml.

#### Example 16

Polymerisation of 4-Me-1-pentene prepolymerised catalyst in Example 13

The catalyst prepared in Example 13 was dispersed to a 150 g/l oil/grease mixture (80+20 vol% of "Parafinium Liquidum 68" from Technol and "Vaselinfett Album" from Technol). The catalyst mud was then fed to a continuous process of two reactors in series: bulk propylene prepolymerisation (9 min residence time at 15°C) and loop bulk propylene polymerisation (1.4 h residence time at 70°C), 670 ppm of hydrogen and 0.1 g/kgpropylene of triethyl aluminum were present.

The catalyst productivity became 6.36 kg/gCat<sub>pure</sub>, or 4.54 kg/gCat<sub>pure</sub>\*h. Process operability was good, and morphology of powder particles, taken out of the lots and from the reactor, showed neither the transparency nor partly fused surface as noticed while using non batch prepolymerised catalyst in Example 14. Inspection of the polymerisation reactor inner surface after 3.5 days of operation did not show sheeting or plugging from this catalyst. Product polymer analyses showed MFR = 28.3, XS = 1.18 wt%, T<sub>m</sub> = 151.7°C. Polymer powder bulk density was 0.416 g/m.

#### Example 17

Propylene polymerisation using a non batch prepolymerized catalyst

110 mg of the catalyst prepared in Example 11 was placed in a 2l inerted steel reactor, and 0.5 mmol TEAL (as 1 M

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heptane solution) and 0.24 bar hydrogen added. Thereafter 1300 ml liquid propylene was added, and 15°C temperature maintained for 8 min. Temperature was then raised to 70°C during 2 min, and maintained for 60 min. Polymerisation was terminated by flashing off the residual propylene. A yield of 340 g polypropylene was obtained. Activity was 4180 g/gCat<sub>pure</sub>. There was no sheeting in the reactor, but a thin almost invisible sticky layer on reactor walls. Powder morphology was acceptable, although some agglomerates and a little fines. Polymer analyses showed MFR = 110, T<sub>m</sub> = 152.0°C, XS = 1.1 wt%.

#### Example 18

##### Prepolymerisation using 1-hexene

10.08 g of supported catalyst, Example 11, was placed in an inerted glass vessel, volume 250 ml, equipped with a Teflon bladed stirrer. Pressure was reduced to 100 mbar and 1-hexene in a connected glass bottle was allowed to evaporate into the vessel through a steel tubing. The 1-hexene pressure in the vessel was ca 150 mbar at 25°C. The 1-hexene connection was closed after 143 min, and the residual 1-hexene removed by evacuation. The weight of prepolymerised catalyst was 11.07 g.

#### Example 19

##### Propylene polymerisation using a 1-hexene prepolymerized catalyst

200 mg of the catalyst prepared in Example 18 was placed in a 2l inerted steel reactor, and 1.0 mmol TEAL (as 1 M heptane solution) and 0.2 bar hydrogen added. Thereafter 1300 mL liquid propylene was added, and 15°C temperature maintained for 8 min. Temperature was then raised to 70°C during 2 min, and maintained for 60 min.

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Polymerisation was terminated by flashing off the residual propylene. A yield of 305 g polypropylene was obtained. Activity was 1670 g/gCat<sub>pure</sub>. There was no deposits or sheeting in the reactor. Powder morphology was still good, although slightly more agglomerates but very little fines as compared to Example 17. Polymer analyses showed MFR = 26, T<sub>m</sub> = 152.4°C, XS=1.1 wt%.

#### Example 20

Prepolymerisation using 3-Me-1-butene

1.00 g of supported catalyst, Example 11, was placed in an inerted glass flask, volume 50 ml, equipped with a magnetic stirrer. A steel bottle containing 3-Me-1-butene (obtainable from Aldrich) was connected using a needle through a septum. A pressure reduction valve was placed in between to control the pressure of 3-Me-1-butene. The flask was first flushed with 3-Me-1-butene to substitute the nitrogen, and then pressure was adjusted to 1.3 bar for 1 hour. The weight increase of the glass flask content was 0.25 g. Thereafter the steel bottle was tilted upside down, and 0.55 g of 3-Me-1-butene added as liquid. The 3-Me-1-butene connection was removed, and the glass flask was stored over the week-end without weight loss. Then the residual 3-Me-1-butene was removed by evacuation at 180 torr for 10 min. The weight of prepolymerised catalyst was 1.51 g.

#### Example 21

Prepolymerisation using 3,3-Me<sub>2</sub>-1-butene

1.03 g of supported catalyst, Example 11, was placed in an inerted glass flask, volume 50 ml, equipped with a magnetic stirrer. A glass bottle containing 3,3-Me<sub>2</sub>-1-butene (obtainable from Aldrich) was cooled in



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a refrigerator to  $-20^{\circ}\text{C}$ , purged with nitrogen to remove traces of oxygen, and stored overnight on 13X molecular sieve. While using a syringe through a septum, 3,3-Me<sub>2</sub>-1-butene was added batchwise to the catalyst containing glass flask until 0.78 g was accumulated. The glass flask was stored over the week-end without weight loss. Residual 3,3-Me<sub>2</sub>-1-butene was removed by evacuation at 185 torr for 10 min. The weight of prepolymerised catalyst was 1.22 g.

#### Example 22

Propylene polymerisation using a 3-Me-1-butene prepolymerized catalyst

160 mg of the catalyst prepared in Example 20 was placed in a 2l inerted steel reactor, and 0,5 mmol TEAL (as 1 M heptane solution) and 0.24 bar hydrogen added. Thereafter 1300 ml liquid propylene was added, and  $15^{\circ}\text{C}$  temperature maintained for 8 min. Temperature was then raised to  $70^{\circ}\text{C}$  during 2 min, and maintained for 60 min. Polymerisation was terminated by flashing off the residual propylene. A yield of 410 g polypropylene was obtained. Activity was 3870 g/gCat<sub>pure</sub>. There were no deposits or sheeting in the reactor. Powder morphology was good, less agglomerates and only a little fines as compared to Example 17. Polymer analyses showed MFR = 55,  $T_m = 152.0^{\circ}\text{C}$ , XS=1.2 wt%.

#### Example 23

Propylene polymerisation using a 3,3-Me<sub>2</sub>-1-butene prepolymerized catalyst

130 mg of the catalyst prepared in Example 21 was placed in a 2l inerted steel reactor, and 0,5 mmol TEAL (as 1 M heptane solution) and 0.25 bar hydrogen added. Thereafter 1300 ml liquid propylene was added, and  $15^{\circ}\text{C}$

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temperature maintained for 8 min. Temperature was then raised to 70°C during 2 min, and maintained for 60 min. Polymerisation was terminated by flashing off the residual propylene. A yield of 355 g polypropylene was obtained. Activity was 3230 g/gCat<sub>pure</sub>. There were no deposits or sheeting in the reactor. Powder morphology was good, still some agglomerates but very little fines as compared to Example 17.

Polymer analyses showed MFR = 80, T<sub>m</sub> = 152.0°C, XS=1.1 wt%.

#### Example 24

Prepolymerisation using 4-Me-1-pentene on a Ziegler-Natta MgCl<sub>2</sub>-supported catalyst

The Ziegler-Natta MgCl<sub>2</sub>-supported catalyst was synthesised following procedures given in patent EP-A-591224, essentially by spray crystallizing a magnesium chloride alcoholate followed by treatment with hot titanium tetrachloride, reacting with an 1,2-dicarboxylic ester, washing in a hydrocarbon and drying.

The catalyst was prepolymerised in an oil mud inside an inerted 50 ml glass bottle containing a magnetic stirrer. An amount of 0.300 g catalyst was dispersed into 14.66 oil, and 0.9 ml 0.5 M heptane solution of TEAL was added. Then 0.31 g of neat 4-Me-1-pentene was added, and the mud was stored over night. This oil mud was used for polymerisation without further treatment. Total weight of mud was 16.00 g, giving a cat<sub>pure</sub> concentration of 1.875 wt%.

#### Example 25

Propylene polymerisation using a 4-Me-1-pentene prepolymerized Z-N catalyst

1.02 g of the catalyst mud prepared in Example 24 was

The catalyst used for prepolymerisation in Example 24 was dispersed into a 2.00 w% oil mud. 0.89 g of this oil mud was placed in a 2l inerted steel reactor, and 3.6 mmol TEAL (as 0.5 M heptane solution), 0.18 mmol cyclohexylmethyldimethoxysilane (as 0.2 M heptane solution), and 0.30 bar hydrogen was added. Thereafter 1300 mL liquid propylene was added, and 15°C temperature maintained for 8 min. Temperature was then raised to 70°C during 2 min, and maintained for 60 min. Polymerisation was terminated by flashing off the residual propylene. A yield of 260 g polypropylene was obtained. Activity was 14610 g/gCat<sub>pure</sub>. There were no deposits or sheeting in the reactor. Powder morphology was acceptable, some fines. Polymer analyses showed MFR = 5.8, XS=1.7 w%.

#### Example 27

Prepolymerisation using 4-Me-1-pentene on a Ziegler-Natta silica-supported catalyst

The Ziegler-Natta silica-supported catalyst was synthesised following procedures given in patent EP-A-949274, essentially by precipitating magnesium chloride onto silica, reacting with titanium tetrachloride and evaporating the slurry medium.

The catalyst was prepolymerised in a oil mud inside an inerted 50 ml glass bottle containing a magnetic stirrer. 1.206 g catalyst and 1.25 mmol TEA (as 0.5 M heptane solution) were dispersed in oil to a total weight of 12.00 g. Then 1.0 g of neat 4-Me-1-pentene was added, and the mud was stored over night. This oil mud was used for polymerisation without further treatment. Total weight of mud was 13.0 g, giving a catpure concentration of 9.28 w%.

#### Example 28

Ethylene polymerisation using a 4-Me-1-pentene prepolymerized Z-N catalyst

1.10 g of the catalyst mud prepared in Example 27 was placed in a 2l inerted steel reactor, and 1.0 mmol TEAL (as 1 M heptane solution) added. A hydrogen pressure of 1.00 bar was added on top of 1.47 bar nitrogen pressure. Thereafter 650 mL liquid isobutane was added, and temperature stabilised at 80°C. Ethylene was then continuously fed, and temperature and pressure controls adjusted to 29.7 bar total pressure at 90°C. Polymerisation was terminated after 47 min by closing the ethylene feed and flashing off the hydrocarbons. A yield of 425 g polyethylene was obtained. Activity was 4163 g/gCat. There were some deposits and sheeting in the reactor. Powder morphology was good, no fines. Polymer analyses showed  $MFR_2 = 0.39$ ,  $MFR_{21} = 12.6$ ,

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density = 0.9576 g/cm<sup>3</sup>.

#### Example 29

Ethylene polymerisation using a non batch prepolymerised Z-N catalyst

98 mg of the catalyst used for prepolymerisation in Example 27 was mixed with 1.0 mmol TEAL (as 1 M heptane solution) and placed in a 2l inerted steel reactor, and 1.02 bar hydrogen was added on top of 1.47 bar nitrogen pressure. Thereafter 650 ml liquid isobutane was added, and temperature stabilised at 80°C. Ethylene was then continuously fed, and temperature and pressure controls adjusted to 30.7 bar total pressure at 90°C.

Polymerisation was terminated after 60 min by closing the ethylene feed and flashing off the hydrocarbons. A yield of 100 g polyethylene was obtained. Activity was 1020 g/gCat. There were no significant deposits or sheeting in the reactor. Powder morphology was good, although some agglomerates, no fines.

Polymer analyses showed MFR<sub>2</sub> = 0.18, MFR<sub>21</sub> = 5.4, density = 0.9549 g/cm<sup>3</sup>.

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Claims

1. A process for preparing polyolefins comprising  
(I) prepolymerising a supported olefin  
polymerisation catalyst with an olefin or olefin  
mixture;

(II) isolating the resulting prepolymerised olefin  
polymerisation catalyst; and

(III) polymerising or copolymerising olefins in the  
presence of the prepolymerised olefin polymerisation  
catalyst;

wherein the olefin or olefin mixture of the  
prepolymerisation is different from that of the  
subsequent olefin polymerisation, wherein the melting  
point or softening point of the polyolefin or olefin  
copolymer resulting from prepolymerisation is at least  
20°C higher than the melting point or softening point of  
the polyolefin or olefin copolymer of the subsequent  
olefin polymerisation and wherein said olefin  
polymerisation catalyst is a metallocene.

2. A process as claimed in claim 1 wherein the melting  
point or softening point of the polyolefin or olefin  
copolymer resulting from prepolymerisation is at least  
30°C higher than the melting point or softening point of  
the polyolefin or olefin copolymer of the subsequent  
olefin polymerisation.

3. The process as claimed in claim 1 or 2 comprising  
two or more metallocenes forming a multi-site catalyst.

4. The process as claimed in claims 1 to 3 wherein the  
pre-polymerization olefin or olefin mixture is one or  
more of propylene, 1-butene, 3-methyl-1-butene, 3,3-  
dimethyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-  
pentene, 4,5-dimethyl-1-hexene, vinyl cyclopentane,

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vinyl cyclohexane, vinyl cycloheptane, allyl cyclopentane, allyl cyclohexane or allyl cycloheptane.

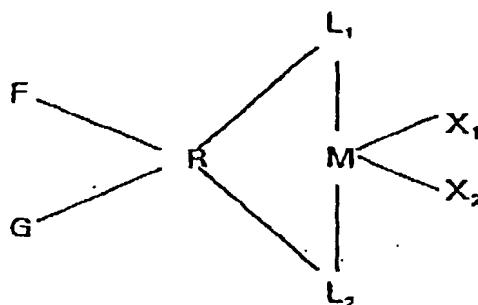
5. The process as claimed in claim 4 wherein the pre-polymerization olefin or olefin mixture is one or more of 3-methyl-1-butene, 4-methyl-1-pentene, vinyl cyclopentane or vinyl cyclohexane.

6. The process as claimed in claims 1 to 5 wherein the support material is silica.

7. The process as claimed in claim 1 wherein said olefin polymerisation catalyst is a supported metallocene catalyst, comprising

A) 90.0 - 99.9 parts by weight of a catalyst support based on a hydrophilic inorganic oxide of an element of main groups II to IV or transition group IV of the Periodic Table or a mixture or mixed oxide thereof, which catalyst support is obtainable by simultaneous reaction with aluminoxanes and with poly-functional organic crosslinkers,

B) 10 - 0.1 parts by weight of a metallocene compound of the formula I



where

M is a metal selected from the group consisting of Ti, Zr, Hf, V, Nb and Ta or an element selected from the group consisting of the lanthanides,

X<sub>1</sub> and X<sub>2</sub> are identical or different and are each a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a

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C<sub>7</sub>-C<sub>20</sub>-alkylaryl group, a C<sub>7</sub>-C<sub>20</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>20</sub>-arylalkenyl group, hydrogen or a halogen atom,

L<sub>1</sub> and L<sub>2</sub> are identical or different and are each an unsubstituted, monosubstituted or polysubstituted monocyclic or polycyclic hydrocarbon radical containing at least one cyclopentadienyl unit which can form a sandwich structure with M,

R is carbon, silicon, germanium or tin,

F and G are identical or different and are each a trimethylsilyl radical of the formula -Si(CH<sub>3</sub>)<sub>3</sub>, where G may also be a C<sub>1</sub>-C<sub>10</sub>-alkyl radical, preferably a C<sub>1</sub>-C<sub>4</sub>-alkyl radical, or a C<sub>6</sub>-C<sub>10</sub>-aryl radical,

characterized in that the supported metallocene catalyst comprising A and B, has an activity of maximum 100 kg, preferably maximum 50 kg, particularly preferred maximum 20 kg polyolefin/g supported catalyst/h.

8. The process as claimed in claim 1 to 7, wherein the pre-polymerization is carried out in gas phase.

9. The process as claimed in claim 1 to 7, wherein the pre-polymerization is slurry phase polymerization in an oil or grease slurry medium.

10. The process as claimed in claim 1, wherein for liquid-phase polymerization of propylene the modification of the supported catalyst is carried out by pre-polymerization of 4-methyl-1-pentene.

11. Use of a modified supported olefin polymerisation catalyst in a process for the manufacture of polyolefins said catalyst being modified by prepolymerisation with an olefin or olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerisation said use reducing reactor fouling.

12. A method of reducing reactor fouling during



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an olefin polymerisation comprising

(I) prepolymerising a supported olefin polymerisation catalyst with an olefin or olefin mixture;

(II) isolating the resulting prepolymerised olefin polymerisation catalyst; and

(III) polymerising or copolymerising olefins in the presence of the prepolymerised olefin polymerisation catalyst;

wherein the olefin or olefin mixture of the prepolymerisation is different from that of the subsequent olefin polymerisation, and wherein the melting point or softening point of the polyolefin or olefin copolymer resulting from prepolymerisation is at least 20°C higher than the melting point or softening point of the polyolefin or olefin copolymer of the subsequent olefin polymerisation.

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(54) Title: MODIFIED SUPPORTED CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

(57) Abstract: A modified supported olefin polymerization catalyst, characterised in that the catalyst is modified by pre-polymerization with an olefin or an olefin mixture different from the olefin or olefin mixture of the subsequent olefin polymerization.

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**Declaration and Power of Attorney**  
U.S. Serial No. 10/089,049  
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I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application (37 C.F.R. § 1.63(d)).

PCT/ GB00/03775

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby authorize my attorney to insert the serial number assigned to this application in this declaration should this number become available before the filing of this declaration.

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the practitioners associated with the firm of LINIAK, BERENATO, LONGACRE & WHITE, LLC to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, and direct that all correspondence and telephone calls be addressed to:

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# DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

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Attorney Docket No: 9100.025

# DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

MODIFIED SUPPORTED CATALYSTS FOR THE POLYMERISATION OF OLEFINS

the specification of which (check one):

( ) is attached hereto, or ( x ) was filed on: 25 March 2002

as U.S. Application Serial No. 10/089049 or PCT

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and (if applicable) was amended on:

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, § 1.56*. I hereby claim foreign priority benefits under *Title 35, United States Code, § 119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	
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